# AFRL-ML-WP-TP-2003-437

# METHODS IN ENTROPIC THERMOMECHANICS

Richard B. Hall

**SEPTEMBER 2000**

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# REPORT DOCUMENTATION PAGE

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| 1. REPORT DATE *(DD-MM-YY)*  September 2000 | 2. REPORT TYPE  Journal Article | 3. DATES COVERED *(From - To)* |
|---|---|---|

| 4. TITLE AND SUBTITLE  METHODS IN ENTROPIC THERMOMECHANICS | 5a. CONTRACT NUMBER  In-house |
|---|---|
|  | 5b. GRANT NUMBER |
|  | 5c. PROGRAM ELEMENT NUMBER  N/A |
| 6. AUTHOR(S)  Richard B. Hall | 5d. PROJECT NUMBER  N/A |
|  | 5e. TASK NUMBER  N/A |
|  | 5f. WORK UNIT NUMBER  N/A |

| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Structural Materials Branch (AFRL/MLBC)  Non-Metallic Materials Division  Materials and Manufacturing Directorate  Air Force Research Laboratory, Air Force Materiel Command  Wright-Patterson AFB, OH 45433-7750 | 8. PERFORMING ORGANIZATION REPORT NUMBER  AFRL-ML-WP-TP-2003-437 |
|---|---|

| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Materials and Manufacturing Directorate  Air Force Research Laboratory  Air Force Materiel Command  Wright-Patterson AFB, OH 45433-7750 | 10. SPONSORING/MONITORING AGENCY ACRONYM(S)  AFRL/MLBC |
|---|---|
|  | 11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)  AFRL-ML-WP-TP-2003-437 |

**12. DISTRIBUTION/AVAILABILITY STATEMENT**
Approved for public release; distribution is unlimited.

**14. ABSTRACT**
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**15. SUBJECT TERMS**
entropy, anelasticity

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT:  SAR | 18. NUMBER OF PAGES  26 | 19a. NAME OF RESPONSIBLE PERSON (Monitor)  Richard B. Hall |
|---|---|---|---|---|---|
| a. REPORT  Unclassified | b. ABSTRACT  Unclassified | c. THIS PAGE  Unclassified | | | 19b. TELEPHONE NUMBER *(Include Area Code)*  (937) 255-9097 |

# Methods in entropic thermomechanics

## Richard B. Hall *

*Air Force Research Laboratory, Materials and Manufacturing Directorate, AFRL/MLBC, 2941 P Strm 136, Wright-Patterson AFB, OH 45433-7750, USA*

Dedicated to Nicholas J. Pagano

**Abstract**

Elements of constitutive model formulation for simple materials within a thermodynamic, finite deformation framework are reviewed. Recent developments in addressing the second law and entropy existence are discussed. Caratheodory-based approaches are emphasized for their simplicity and ease of interpretation. An original treatment of finite thermoviscoelasticity is developed in this context. A broadened Caratheodory-based entropy is proposed, and compared to recent work of Casey (Casey J., On elastic–thermo-plastic materials at finite deformations. Int J Plast, 14, 173–91.). Frame indifference, objective rates, and spins are briefly addressed, introducing application of the broadened framework to (cited work in) finite thermoviscoplasticity. Fundamental references are provided. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Entropy; Anelasticity

## 1. Introduction

*The student is usually introduced to the concepts of thermodynamics...in a way which does violence to credibility. (Serrin [2], quoting Cardwell.)*

### 1.1. Simple materials

This paper is primarily concerned with the thermo-mechanics of continuum simple materials:

A material is said to be *simple* if its response at particle $\vec{X}$ at time $t$ is determined by the history of the local deformation at $\vec{X}$ and the history of the temperature at $\vec{X}$ [up to] time $t$... and generally the current value of the temperature gradient $\vec{g}(t)$ ([3]; cf. [4]).

The modeling associated with "simple materials with memory" traditionally involves hereditary functionals, i.e. integrals over the time history of the deformation.

Here internal variable representations are considered equivalently viable. The internal variables **a** may be written as dependent on the histories of the Lagrange strain **E** and temperature $\theta$, and the present temperature gradient $\vec{g}(t)$, i.e., dependent on the controllable, or at least observable, variables (cf. [5–8]):

$$\mathbf{a}(t) = \underset{s=0}{\overset{\infty}{\mathbf{A}}}(\mathbf{E}(t-s), \theta(t-s), \vec{g}(t)) \tag{1}$$

where the functional expression $\underset{s=0}{\overset{\infty}{\mathbf{A}}}(\cdot)$ indicates dependency on the temporal argument $(t-s)$ over the indicated range of the parameter $s$. Internal variables cannot generally be observed during a process, but are made to evolve by changing the controllable variables. Associations of the internal variables with evolving average microstructural features are, however, often possible. Internal variable treatments usually employ rate functions to characterize evolutions of the dependent variables.

### 1.2. Notation

$\vec{X} = X_I \vec{E}_I$ (repeated indices are summed) denotes a given material point, with location assigned relative to the *material (reference) coordinate system* with ortho-normal base vectors $\vec{E}_I$ ($I = 1, 2, 3$). The position of such a point at time $\tau$ during its motion is $\vec{y} = \vec{y}(\vec{X}, \tau) = y_i \vec{e}_i$,

* Tel.: +1-937-255-9097; fax: +1-937-656-4706.

*E-mail address:* richard.hall@afrl.af.mil (R.B. Hall).

relative to the *current (spatial) system* with ortho-normal base vectors $\vec{e}_i$ ($i = 1, 2, 3$). The components of the *deformation gradient* $\mathbf{F}$ are $F_{iJ} \equiv \partial y_i / \partial X_J$. Subscript (a)s indicates (anti)symmetry. Superscript T denotes the transpose. $A_{ik}B_{ik} = A_{ki}^{\mathrm{T}}B_{ik} \equiv \mathbf{A}^{\mathrm{T}} \cdot \mathbf{B} \equiv \mathrm{tr}(\mathbf{A}^{\mathrm{T}}\mathbf{B})$. For $(\tilde{\mathbf{T}}, \mathbf{T})$ second-rank tensors referred to the reference and current configurations, respectively, $\mathrm{DIV}\tilde{\mathbf{T}} \equiv \vec{\nabla}_0^{\mathrm{T}}\tilde{\mathbf{T}}$ has components $\partial \tilde{T}_{IJ}/\partial X_I$, and $\mathrm{div}\mathbf{T} \equiv \vec{\nabla}^{\mathrm{T}}\mathbf{T}$ has components $\partial T_{ij}/\partial y_i$. The terminology and notation are from standard texts such as Malvern [9].

## 2. Deformations, energy balance

The first law of thermodynamics (energy balance) for a continuum is expressed, relative to the current configuration (e.g. [9]):

$$
\begin{aligned}
\dot{\mathbf{E}} &= \frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\varepsilon\,\mathrm{d}V = \frac{\mathrm{d}}{\mathrm{d}t}\int_V (\tfrac{1}{2}\rho\vec{v}^{\mathrm{T}}\vec{v} + \rho u)\mathrm{d}V \\
&= \dot{P}_{\mathrm{in}} + \dot{Q}_{\mathrm{in}} \\
&= \left[\int_S \vec{t}^{\mathrm{T}}\vec{v}\,\mathrm{d}S + \int_V \rho\vec{b}^{\mathrm{T}}\vec{v}\,\mathrm{d}V\right] + \left[\int_V \rho r\,\mathrm{d}V + \int_S -\vec{n}^{\mathrm{T}}\vec{q}\,\mathrm{d}S\right]
\end{aligned}
\tag{2}
$$

E is the total of the internal and kinetic energies of the body; the overdot and $\frac{\mathrm{d}}{\mathrm{d}t}$ both denote the material derivative ($\frac{\partial}{\partial t}$ with $\vec{X}$ fixed). $\dot{P}_{\mathrm{in}}, \dot{Q}_{\mathrm{in}}$ are the inputs of mechanical and thermal energy, corresponding to the bracketed terms beneath. $\rho, \varepsilon, u, \vec{t}, \vec{b}, \vec{v}, r, \vec{q}, \vec{n}$ are, respectively, the mass density, specific total energy, specific internal energy, traction, specific body force, velocity, specific rate of heat supply, surface heat flux, and outer unit normal, and $V$ and $S$ are body volume and material surface. Applications of the divergence theorem, material derivative and the equations of motion [9] result in the local forms (assuming sufficient smoothnesses for the derivatives to exist):

$$
\rho\dot{\varepsilon} = \mathrm{div}(\mathbf{T}\vec{v} - \vec{q}) + \rho\vec{b}^{\mathrm{T}}\vec{v} + \rho r
\tag{3}
$$

$$
\rho\dot{u} = \mathbf{T} \cdot \mathbf{L} - \mathrm{div}\vec{q} + \rho r
\tag{4}
$$

$\mathbf{L}$ is the velocity gradient, with components $L_{ij} = \partial v_i / \partial y_j$. The components $T_{ij}$ of the Cauchy stress $\mathbf{T}$ refer[1] to the force acting on a plane with normal $\vec{e}_i$, in the direction $\vec{e}_j$. Eq. (3) and the equations of motion produce (4). Total and internal energy *functions of state*[2]

---

[1] Malvern [9]. The convention followed by e.g. Truesdell and Noll [12] is the transpose.

[2] The existences of total and internal energy functions are discussed by e.g. [2,9,10,11,13]. Suitably broad concepts of 'state' (global, local) are employed to identify history-dependent quantities as state functions.

are required to recover the balance and interconvertibility of heat and work for cyclic processes (cyclic integrals of $\mathrm{d}\varepsilon$, $\mathrm{d}u$ vanish). The energy rates balance the mismatch of heating and working rates for noncyclic processes.

Eqs. (2)–(4) are referred to the initial configuration by employing conservation of mass and the relation between oriented area elements in the reference vs. current configurations [9]:

$$
\rho_0/\rho = \mathrm{d}V/\mathrm{d}V_0 = J
\tag{5}
$$

$$
\vec{n}^{\mathrm{T}}\mathrm{d}S = \frac{\rho_0}{\rho}\vec{N}^{\mathrm{T}}\mathbf{F}^{-1}\mathrm{d}S_0
\tag{6}
$$

$\rho_0, \mathrm{d}V_0, \mathrm{d}S_0, \vec{N}$ are, respectively, the mass density, volume element, surface element, and external normal to the surface in the reference configuration, and $J$ is the Jacobian determinant, $J \equiv \det\mathbf{F}$. Analogues to (4) are then obtained, e.g.

$$
\rho_0\dot{u} = \begin{cases} \mathbf{T}^0 \cdot \dot{\mathbf{F}} \\ \tfrac{1}{2}\tilde{\mathbf{T}} \cdot \dot{\mathbf{C}} \\ \tilde{\mathbf{T}} \cdot \dot{\mathbf{E}} \end{cases} - \mathrm{DIV}\vec{q}_0 + \rho_0 r
\tag{7}
$$

where

$$
\vec{q}_0 \equiv \frac{\rho_0}{\rho}\mathbf{F}^{-1}\vec{q}
\tag{8}
$$

$$
\mathbf{T}^0 \equiv \frac{\rho_0}{\rho}\mathbf{F}^{-1}\mathbf{T}, \quad \tilde{\mathbf{T}} \equiv \frac{\rho_0}{\rho}\mathbf{F}^{-1}\mathbf{T}(\mathbf{F}^{-1})^{\mathrm{T}}
\tag{9}
$$

$$
\mathbf{C} \equiv \mathbf{F}^{\mathrm{T}}\mathbf{F}, \quad \mathbf{E} \equiv \tfrac{1}{2}(\mathbf{C} - \mathbf{I})
\tag{10}
$$

and the following relationships are employed [9]:

$$
\mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1}
\tag{11}
$$

$$
\mathbf{D} \equiv \mathbf{L}_s = \tfrac{1}{2}\mathbf{F}^{-\mathrm{T}}\dot{\mathbf{C}}\mathbf{F}^{-1} = \mathbf{F}^{-\mathrm{T}}\dot{\mathbf{E}}\mathbf{F}^{-1}.
\tag{12}
$$

$$
\mathbf{A} \cdot (\mathbf{BC}) = \mathbf{C} \cdot (\mathbf{AB}) = (\mathbf{CA}) \cdot \mathbf{B}
\tag{13}
$$

$\mathbf{T}^0, \tilde{\mathbf{T}}, \mathbf{C}, \mathbf{E}, \mathbf{D}$ are tensors respectively referred to as the first and second Piola–Kirchhoff stress, the right Cauchy–Green deformation, the Lagrange strain and the rate of deformation. $\mathbf{I}$ is the unit tensor. $\mathbf{L}_s$ is the symmetric part of $\mathbf{L}$.

The energy balance appears in Section 3.3 as

$$
\rho_0\dot{u} = \tilde{\mathbf{T}} \cdot \dot{\mathbf{E}} + \dot{Q}_0; \quad \dot{Q}_0 \equiv -\mathrm{DIV}\vec{q}_0 + \rho_0 r
\tag{14}
$$

## 3. Entropy and the second law

### 3.1. Dissipation inequality

Coleman and Noll [14] originated a now standard procedure (e.g. [12,15–17]) for deducing constitutive equations through application of a statement of the second law of thermodynamics. The following inequality (called the global C–D–T–T, or Clausius–Duhem–Truesdell–Toupin, inequality by Man [18,19]) is postulated for irreversible or reversible processes, *assuming the existences* of (specific) entropy $\eta$ and absolute temperature $\theta$, and extensivity of entropy:

$$\frac{d}{dt}\int_V \rho\eta\,dV \geq \int_S \frac{-\vec{n}\cdot\vec{q}}{\theta}\,dS + \int_V \frac{\rho r}{\theta}\,dV \tag{15}$$

Assuming the necessary smoothness properties, the divergence theorem is applied, with the resulting local form of the C–D–T–T inequality:

$$\gamma \equiv \dot{\eta} - \left[ -\frac{1}{\rho}\mathrm{div}\frac{\vec{q}}{\theta} + \frac{r}{\theta} \right] \geq 0 \tag{16}$$

$\gamma$ is termed the *specific rate of production of entropy*,[3] and identifies an irreversible process when nonzero. (Truesdell and Toupin [22], Sections 256–258, interpret $\gamma$ as irrecoverable work and/or heat flow through a temperature gradient.) Substitution for $\dot{Q} \equiv -\mathrm{div}\vec{q} + \rho r$ from the first law (4) produces

$$\gamma = \dot{\eta} - \frac{1}{\theta}\left( \dot{u} - \frac{1}{\rho}\mathbf{T}\cdot\mathbf{L} \right) - \frac{\vec{q}^{\mathrm{T}}\vec{g}}{\rho\theta^2} \geq 0, \quad \vec{g} \equiv \vec{\nabla}\theta \tag{17}$$

Defining the Helmholtz free energy

$$\psi \equiv u - \theta\eta \tag{18}$$

results in the *dissipation inequality*,

$$\theta\gamma = -\dot{\psi} - \eta\dot{\theta} + \rho^{-1}\mathbf{T}\cdot\mathbf{L} - (\rho\theta)^{-1}\vec{q}^{\mathrm{T}}\vec{g} \geq 0 \tag{19}$$

Postulating the independent variables for $\psi$ (including possible history-dependence, see Section 5.3), employing the chain rule expression for $\dot{\psi}$ assuming sufficient smoothness, then requiring (19) to be valid for arbitrary rates results in expressions for $\mathbf{T}$ and $\eta$ in terms of derivatives of the free energy.

*It is doubtful whether a sufficiently smooth entropy density function [to accommodate the described C–D–T–T-based treatment] could be generally valid for*

all classes of materials studied in thermomechanics [19].

### 3.2. Modern treatments

*For even more complex [than Navier–Stokes fluids] materials, the possibility of deriving internal energy and entropy from the laws of thermodynamics is arguably an open question [2].*

It is emphasized that works described under this heading consider dynamic, spatially heterogeneous processes for heterogeneous material systems. The present section is intended as a guide to selected sources for the interested reader. General references and bibliographies for this subject are found in Man [19], Serrin [2,23], Silhavy [13], Coleman and Owen [11], Truesdell [16], Owen [24] and Hutter [25]. The latter reference and Silhavy ([13], Chapter 12) touch on differences between two main schools of development, so-called "irreversible thermodynamics" and "rational thermodynamics." (The "rational" school is the main focus of the present review. The machinery of the "irreversible" school was originally predicated on nearby equilibrium states, e.g. [26–27]. Recent extensions are discussed in [108–110].)

Modern treatments of the mathematical foundations for the existence and properties of entropy, and precise statements of the second law, exploit concepts of, e.g. real and functional analysis, set theory, topology and measure theory. Three issues are of primary interest here:

1. Precise statements of the global second law for *thermodynamic systems* (physical, volumetric entities such as bodies, sub-bodies, gases), and consequent implications for the existence of entropy for the system.
2. Local statements of the second law, implying the existence of entropy at a continuum point; further, whether the entropy functions possess the differentiabilities required to derive results for the response functionals as described[4] in Section 3.1.
3. The relationship between the aforementioned global and local statements and properties.

"The basic idea that, even for systems with memory, a thermodynamical inequality of the Clausius type should imply the existence of an entropy function is found in an important paper of W. A. Day [28]" [11]. This paper and Day [29] also show foundational efforts toward the

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[3] The symbol $\dot{\gamma}$ is used in Valanis [20] and Hall [21].

[4] See Sections 3.3, 5.1, 5.3 for illustrations. Coleman and Owen [11] employ $u$, $\mathbf{F}$, and $\vec{\beta} \equiv \vec{g}/[\rho\theta]^2$ as state variables, and extract the expected restrictions on constitutive functions directly from their second law, as opposed to Eq. (19). As noted in the sequel, the existence of $u$ is deduced in [11] from a cyclic form of the first law.

modern heating measures later devised by the authors of global treatments, and composition arguments adopted by both global and local treatments. Processes must start and finish in equilibrium states; a second law is expressed for corresponding closed paths. The existence of absolute temperature is assumed. (Discussions are provided in [6,30].) Also emphasized by Owen [24] is the work of Noll [31], for introducing concepts from mathematical systems theory.

Coleman and Owen [11,32,33] develop a general theory of *actions* on associated *systems,*[5] addressing *local* thermodynamics applications. For "simple material elements," processes $P$ are defined by piecewise continuous functions of time $(\mathbf{L}(\tau), h(\tau), \vec{\beta}(\tau))$, with $\vec{\beta}(\tau) \equiv \vec{g}(\tau) / [\rho(\tau)\theta(\sigma_\tau)]^2$, $h(\tau) \equiv r(\tau) - [\rho(\tau)]^{-1} \mathrm{div} \vec{q}(\sigma_\tau)$. The stress, absolute temperature, and heat flux are given, continuous functions of the state $\sigma_\tau$; these state functions are deduced by the treatment to obey restrictions (which provide the stress, temperature and dissipation relations) required by the second law. The stress is also assumed time-differentiable. The *actions* $\mathscr{w}$ and $\mathscr{s}$ are defined as

$$\mathscr{w}(P, \sigma) = \int_0^t \rho^{-1} \mathbf{T}(\sigma_\tau) \cdot \mathbf{L}(\tau) \mathrm{d}\tau + \int_0^t h(\tau) \mathrm{d}\tau \tag{20}$$

$$\mathscr{s}(P, \sigma) = \int_0^t \frac{h(\tau)}{\theta(\sigma_\tau)} \mathrm{d}\tau + \int_0^t [\vec{q}(\sigma_\tau)]^T \vec{\beta}(\tau) \mathrm{d}\tau \tag{21}$$

The statements of the (first, second) laws are that the actions $(\mathscr{w}, \mathscr{s})$ have the (conservation, Clausius) properties at one point in the state space; this framework also requires the assumption of *approximate accessibility*, i.e. every state can be reached[6] from every other state. An action has the (conservation, Clausius) property at a point of the state space if it is approximately (zero, non-positive) for each nearly cyclic process initiated from the point. A nearly cyclic process maps a point of the state space to a point within an arbitrarily small neighborhood of the original. The framework of approximate cycles permits treatment of materials with memory properties, for which exact cycles may be scarce. The (conservation, Clausius) properties for $(\mathscr{w}, \mathscr{s})$ can be motivated if one assumes the validities of Eqs (4) and (16) with $(u, \eta)$ regarded as path-independent functions of state; the treatments now described seek to prove such functions exist.

Underlying the described framework is the assumption of an abundance of nearly cyclic processes (e.g. it is deduced that given a state where $\mathscr{s}$ has the Clausius property, any state accessible from it also conveys this property). Coleman and Owen [34] thus modify the accessibility requirement; the existence of only one base

state (e.g. an annealed state in a metal) is required, from which all others may be reached. The second law is then restated without recourse to cycles: The action $\mathscr{s}$ must be upper bounded, from the base state to all other states (including the base state), via all processes connecting the states. The previously described Clausius property is implied by the bound.

Both frameworks are applied to a material *point* associated with a *system*, an ordered pair $(\Sigma, \Pi)$ of collections $\Sigma$ of states $(\sigma)$ and $\Pi$ of processes $(P)$; each process $P$ determines a continuous mapping of states of $\Sigma$ to states of $\Sigma$. For any processes such that the range of a process is the domain of another process, $\Pi$ must contain a composite process which maps the domain of the first process to the range of the second process. Actions have the properties: (1) that the value of an action of a composite process is the sum of the values of the actions on the component processes; (2) for each $P$ in $\Pi$, the action is continuous on the domain of $P$. The described properties, and the assertion that the system obeys the second law, lead to the existences of: (a) internal energy functions having all states in their domains, and (b) entropy functions having in their domains a set of states which is dense in the space of states, i.e., all neighborhoods contain such states[7]. The first law is automatically satisfied by simple material elements ([11], p. 44).

The simple material elements addressed by the theory include thermoelastic elements, viscous fluid elements, elements with fading memory, and elements with internal variables (where the evolution rates of the internal state variables are given by functions of state variables only, i.e. no rates). Postulated state dependencies and topologies entering the action $\mathscr{s}$ for these specific materials permit construction of path-independent $\mathscr{s}$-like integrals parametrized by *instantaneously controllable* variables, inferring the desired instantaneous differentiability properties for the entropy. Virtually all previously existing results based on the local C–D–T–T inequality, with assumed, differentiable entropy, are recovered. Elastic–perfectly plastic materials in one space coordinate are treated by similar means in Coleman and Owen [32,35].

Applying strategies related to [34], Lucchesi and Silhavy [36] investigate rate-independent, finite deformation thermoelastoplastic models. Materials considered are initially isotropic and obey the combined hardening rule of Reed and Atluri [37], which includes as special cases the hardening rules of Melan, Prager, and Armstrong and Frederick. Conditions for satisfaction of both the second

---

[5] In Section 3.2, the word 'system' without a modifier (e.g. 'thermodynamic') is reserved for the state space–process space pair introduced by Coleman and Owen [11], described in the sequel.

[6] One can get arbitrarily close to any state via the set of processes $\Pi$.

[7] $u$ exists at *every* state of a simple material element ([11], p. 43); in the cases of elements with internal variables, or elements with fading memory, entropy may not ([11], p.11). The base state $\sigma_0$ is in the domain of the entropy function, and all processes in $\Pi$ from $\sigma_0$ map to states where entropy exists ([11], pp. 12, 46; [34], pp. 175–177, 181); such states are arbitrarily close to any given state ([34], pp. 173–174).

law and a nonisothermal generalization of Il'yushin's condition are given, and features of the set of (i.e., non-unique) entropy functions satisfying the local second law are obtained.

Selected contributions toward developing *global* thermodynamic frameworks having the aforementioned properties are Day [28,29] as previously described, Serrin [10,38], Silhavy [39,40] and Coleman, Owen and Serrin [41]. For further references see the beginning of this section.

Unaddressed by the described work of Coleman and Owen was the question of whether a classical *global* statement or statements of the second law, which apply to bodies, actually imply the *local* results. The first difficulty posed by this question was how to, if possible, unambiguously and precisely state mathematically the various versions of 'the' second law. One could then also deduce which statements implied others, which were most or least restrictive or general, and potentially even deduce an improved statement or statements. Precise statements of the global second law are now realized, through employment of the 'accumulation function' of Serrin [38] and the equivalent "heating measure" treatment of Silhavy [39, 40], deduced independently. Silhavy [13] (p. 126) notes that assuming the heating measures of bodies in a space ('collection') of bodies are additive, with one of the bodies in the space being a reversible fluid, produces equivalence between four statements of the second law (Carnot, Kelvin and two of Clausius), while the absolute temperature must be an increasing function of the empirical temperature.[8] Coleman, Owen and Serrin [41] express their framework in terms of 'approximate cycles' in a way similar to the development of Coleman and Owen [11].

The accumulation function $Q(P, L)$ represents the net heat transferred to the thermodynamic system during the process $P$ at hotness levels not exceeding $L$. With $\bar{W}(P)$ identified as the total (or net) work done on the environment by the process $P$, Serrin [2] states the second law as follows:[9]

*If $\bar{W}(P) > 0$ for a cyclic process $P$ of a thermodynamical system $S$, then there is some hotness level $L_0$ for which $Q(P, L_0) < 0$* (22)

This corresponds to an interpretation of Carnot's statement of the second law [13]: "To produce a positive amount of work in a cyclic process, the body must not only absorb heat (this follows from the first law); it must also emit some (perhaps very small) amount of it." The

primitive variables are here considered to be *work, heat* and *hotness*. Hotness is a totally ordered set with associated strictly increasing maps, onto the real numbers, called *temperature scales*. The accumulation function "provides the crucial link between heat and temperature in the theory, and codifies the observational evidence that heat supplied at one temperature is very different than heat supplied at another." [2].

The *accumulation inequality* (implied by the second law) is expressed as, "for every *cyclic* process $P$ of every thermodynamic system" [2],

$$\bar{A}(P) \equiv \int_0^\infty \frac{Q(P, L)}{\theta^2} \, d\theta = \int_0^\infty \frac{dQ(P, L)}{\theta} \leqslant 0 \qquad (23a)$$

$$Q(P, L) = 0 \text{ when } L \prec L_\mathrm{l}, \qquad (23b)$$

$$Q(P, L) = \bar{Q}(P) \text{ when } L \succ L_\mathrm{u}. \qquad (23c)$$

$\bar{Q}(P)$ is the net heat supplied to the thermodynamic system during the process. Heat exchange with the environment occurs between lower and upper hotness bounds $L_\mathrm{l}$ and $L_\mathrm{u}$. Any temperature scale $\theta$ which conforms to (23) is at most a positive constant multiple of any other; (23) identifies absolute temperature. If there exists a function $S$ such that $\Delta S \geqslant \bar{A}(P)$ for each (generally non-cyclic) process $P$ and associated states, then $S$ is an entropy function corresponding to the specified state structure. The treatment of [41] employs the accumulation integral $\bar{A}$ of Eq. (23) as an action, in analogy to $\partial$ of Eq. (21). A systems framework and accessibility assumptions analogous to those of Coleman and Owen [11] produce similar entropy existence conclusions when applied to bodies and subbodies.

A partially unresolved issue is that the machinery of the previously described global thermodynamics does not directly imply local results. "*Unlike material bodies, material elements are not 'thermal [thermodynamic] systems' — an accumulation function in general cannot be defined for a process that a material element undergoes*" [19]. A substantial step toward unifying global and local treatments is made by Owen [42]. He notes that "the states and processes of a subbody are accessible only via states and processes of the entire body"; any change of state of a subbody causes a change of state of the larger body. He therefore adopts the structure of a "sheaf" of *algebraic semi-systems*. The sheaf incorporates rules for both translations of properties between parts of the body (or the body) and their subparts, as well as direct translations between different sublevels; i.e. $(A \leftrightarrow B \leftrightarrow C) \Rightarrow (A \leftrightarrow C)$. Local states and processes are unique projections from all parts which contain the point. Semi-systems $(\Sigma, \Pi)$ have the property of accessibility of all states $\sigma \in \Sigma$, via processes $P \in \Pi$, from at

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[8] Empirical temperature is a scale which increases with hotness; see also Silhavy [13], p. 109.

[9] A more general statement [41] modifies Eq. (23) for approximate cycles: roughly, a system obeys the second law iff for each $\varepsilon > 0$, each state has a neighborhood where $\bar{A} < \varepsilon$ whenever a process maps the state to another within the neighborhood.

least one base state, a property thus postulated at global and subbody levels of the sheaf; it projects to the points. Composition of processes and additivity of actions are again incorporated in the semi-systems. The global second law is taken to be the property of boundedness of an action; a bounded local action is deduced from the described framework. When the global action is postulated to be the accumulation integral $\bar{A}$ of Eq. (23), the action $\mathcal{A}$ of Eq. (21) is deduced locally.[10] The existence of entropy following from the global second law is thus translated to local existence. An interesting problem for further study is the extent to which the global–local analysis in [42], set in the framework of algebraic semi-systems, covers the types of materials treated only locally and in the context of systems with approximate accessibility in Coleman and Owen [11]. The global systems considered by Owen [42] possess extensive entropy functions in a setting that encompasses heterogenous thermodynamical processes.

Finally, an alternate approach to the subject may be noted. Man [18] extends, to inhomogeneous processes, treatments by Truesdell (e.g. [44–46]) based on work inequalities. The inequalities are applied to an entire body or any subvolumes. The treatment assumes the existence of entropy for the body or subvolumes. Man finds that the global C–D–T–T inequality implies his inequality, so his inequality is at most as restrictive as the C–D–T–T. Other conclusions are that it implies Serrin's [38] interpretations of the classical statements of the second law, and for 'smooth processes' assuming the validity of the Fourier inequality, it implies the local C–D–T–T inequality. The level of smoothness required is the same as that required to go directly from the global C–D–T–T form to the local form.

### 3.2.1. Classical material systems

Serrin ([2], Part II) specializes the global methods previously described to "classical material systems." The associated modeling employs: processes represented by paths in a state space; an absolute temperature $\theta$ corresponding to each state ($\theta$ may itself be a state variable); connectedness of the state space; differential forms, with continuous coefficient functions, for heating $q$ and working $w$ as follows ($\sigma$ denotes a state):

$$q = \sum_{i=1}^{k} q_i(\sigma)\mathrm{d}\sigma_i; \quad w = \sum_{i=1}^{k} w_i(\sigma)\mathrm{d}\sigma_i \tag{24}$$

These forms are integrated over a path in state space to give the total quantities for the process. Existences of continuously differentiable internal energy $U$ and entropy $S$ functions follow from a cyclic statement of the first law, the accumulation inequality (23), and consideration of closed paths between two states.

The entropy production is zero at the quasistatic limit, the condition when (24) is assumed valid; i.e., the expressions (23) and $\Delta S \geqslant \bar{A}(P)$ become equalities,[11] and $\mathrm{d}S = \mathrm{d}Q/\theta$. Correspondingly, from (24) it is observed that reversing an increment along a given state path will result in heating and working increments which are the negatives of those in the forward direction. These are the conditions for a reversible process [2]. The model is therefore compatible only with materials and processes displaying reversible behaviors in the quasistatic limit. Plastic deformation, for example, is associated with history-dependent, irreversible[12] micro-structural rearrangements; entropy production should be admitted in corresponding models, regardless of rates.[13] "Whether a quasi-static process can arise from material processes $P_n$ with the limiting behavior given by the previous formulas,[14] is a problem which must be faced with the same honesty as for reversible processes" [2].

### 3.3. Caratheodory frameworks

The quotation which opened the previous section indicates issues in the theoretical foundations of thermodynamics, regarding the generality of materials and processes accommodated. The simpler methods described in this section are justified by the acceptable accuracies of conclusions derived from them. The quasistatic entropy production may be non-zero in these approaches.

The approaches described here are considered by some authors (e.g. [13,30], noting Section 3.3.1 below regarding irreversible processes) applicable to quasi-thermostatics only, i.e. conditions near thermodynamic equilibrium. Entropy and absolute temperature again appear as derived, rather than primitive, quantities. Arguments for the quasistatic limitation, by the authors cited, involve the treatments of absolute temperature and extensivity of entropy (Section 3.3.1). Different opinions are recorded by e.g., Boley and Weiner [47] and Nemat-Nasser [5–7,106], who treat nonequilibrium, inhomogeneous processes. See also Silhavy [13], p. 109, indicating limitations exist for *any* treatment incorporating the concept of temperature.

Nonequilibrium systems may certainly be modeled, in association with e.g. the concept of temperature, when the "method of local state" applies (e.g. [17,48]): the relaxation times inherent to local thermodynamic equilibrium should be much shorter (e.g. order of atomic vibration periods) than the characteristic times of the macroscale deformations and processes considered. The

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[10] Due to an unpublished result of Serrin [43].

[11] Note e.g. the next to last equation of [2], p.59.

[12] Reversing the path of controlled variables does not cause retracing of the path of dependent variables, which may include the microstructure.

[13] Cf. the rate-independent treatment of Lucchesi and Silhavy [36].

[14] The specific formulas referred to give the heating and working quasistatic limits as path integrals of Eq. (24).

local behavior can thus be considered as a succession of quasi-equilibrium states. The term 'quasi-equilibrium' refers to the presence of temporal derivatives at the macroscale required for e.g. rate-dependent deformation. [The present discussion should not be confused with the alternative approach of, e.g. [26,27]; see e.g. Eq. (21) of the former.]

### 3.3.1. Theorem of Caratheodory. Application to total deformation and internal variables

Thermodynamic states for the materials of interest are assumed specified by $(\mathbf{E}, \vartheta; \mathbf{a})$.[15] $\mathbf{E}$ is the Lagrange strain tensor; $\mathbf{a}$ represents internal variables, which may have arbitrary tensorial order but usually have order two or zero (scalar). $\vartheta$ denotes *empirical temperature*, a function which increases with hotness. An energy variable, e.g. $u$, might be used instead of $\vartheta$ [49–51]. A semicolon separates the controllable variables from the uncontrollable internal variables $\mathbf{a}$ [5–7]. The internal energy density and stress are assumed to be single-valued functions of $(\mathbf{E}, \vartheta, \mathbf{a})$.

Casey [1] offers an equivalent approach to that of this section without directly incorporating Caratheodory's theorem. Although this equivalence is not noted there, the process of deduction employed there offers an alternative basis for what follows here. Coleman and Gurtin [52] take a reverse approach to the present, assuming entropy and absolute temperature as primitive concepts. Other features are nearly identical.

It is assumed that irreversibilities of processes without heat sources or heat flux through the boundary ($\dot{Q}_0 = 0$) derive only from thermodynamic forces acting through changes d$\mathbf{a}$ of the internal variables. Thus when $\mathbf{a}$ is constant, all associated irreversibilities vanish. It is understood that the internal variables $\mathbf{a}$ can be fixed mathematically, whether or not this can be realized during any given physical process, without consequence to the treatment. For $\mathbf{a}$ fixed, a suitably small neighborhood on the associated hyperplane is assumed to present a continuum of accessible elastic transitions [6].

Caratheodory established a theorem for the integrability of linear differential forms, which he used to formulate a basis for the existence of a universal (thermodynamic, absolute) temperature and entropy [20,47,51,53]. Bernstein [54] and Truesdell [16,55] note that the original proof of the theorem is open to certain criticisms, which they also note are surmountable. Numerous proofs of the theorem have been offered (e.g. [54], with footnote of Truesdell [55], p. 117; [20,30,50,51,56,57]).

Caratheodory's theorem can be applied to the internal variable frameworks described here [5–7,20,47,57,106]. As noted by the cited authors, the variables associated with irreversibilities must be held fixed when integrating

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[15] Omission of the temperature gradient is discussed in Section 5.3.

the first law. This conclusion agrees with the assessment by other authors (e.g. [13,51]) that Caratheodory's approach may be applied only to reversible processes. It is assumed [49,51] that during such a reversible process the changes of state *can* be completely specified by a set of *deformation coordinates* ($\mathbf{E}$ here, for $\mathbf{a}$ fixed) and just one *nondeformation coordinate* (e.g. $\vartheta$ or $u$); furthermore, that each fixed set of deformation coordinates is associated with a continuous range of possible states (i.e. the nondeformation coordinate), and continuous variation of the deformation coordinates results in a continuous variation of the range of possible states. All functions entering the differential form must be once continuously differentiable [55,56]. It is lastly, and importantly, assumed that for processes under consideration ('locally reversible' [47]), the internal energy is always given by the same equation of state, for irreversible or reversible processes. Application of Caratheodory's theorem then produces relations between functions of state which are assumed valid for any transition, reversible or irreversible.

Caratheodory's statement of the second law can be expressed in relation to the present framework as follows (cf. [7,20,47,56,57]):

*At an arbitrary state $\{\bar{\mathbf{E}}, \bar{\vartheta}; \bar{\mathbf{a}}\}$ and point $\overset{+}{X}$, there exist arbitrarily close states inaccessible by locally adiabatic processes, for fixed $\mathbf{a} = \bar{\mathbf{a}}$* $\qquad$ (25)

Statement (25) addresses *local* (point) elastic transitions. It may be understood in terms of local Taylor series representations of actual, generally inelastic, transitions. Responses to arbitrary, incremental changes of the controllable variables may be decomposed into the corresponding elastic responses ($\mathbf{a}$ fixed) and the additional responses due to the changes of internal variables. Similarly, by fixing internal variables *globally*, considering adiabatic transitions and states of the body, statement (25) becomes Caratheodory's second law as applied to elastic transitions of bodies.

Statement (25), even when the restriction to elastic transitions is removed, is an incomplete statement of the second law in comparison with the classical statements of Clausius, Kelvin, Carnot and Plank; it provides no information regarding *which* states are inaccessible. Caratheodory's inaccessibility statement may be referred to as the 'first part' of the second law; identification of the inaccessible states involves an inequality and is referred to as the 'second part' of the second law (e.g. [1,7]). The latter requirement is addressed in a forthcoming subsection. Reconciliation of statements similar to (25) with the classical statements of the second law is given by Buchdahl [56]; see also [7,30,51,58].

Caratheodory's theorem for integrability of linear differential ('Pfaffian') forms may be stated as follows (cf. [47], [55] p. 117 footnote, [20,51,53]):

_If in every neighborhood including an arbitrary point $\bar{\xi}_0$, there exist points $\bar{\xi}$ which are inaccessible along curves satisfying the differential equation_

$$\sum_{\alpha=1}^{n} P_\alpha(\xi_1, \ldots, \xi_n)\mathrm{d}\xi_\alpha = 0, \tag{26}$$

_where the $P_\alpha(\xi_1, \ldots, \xi_n)$ are single-valued, continuously differentiable functions of the arguments, the linear differential form possesses an integrating factor $\lambda(\xi_1, \ldots, \xi_n)$ such that_

$$\frac{1}{\lambda(\vec{\xi})}\sum_{\alpha=1}^{n} P_\alpha(\vec{\xi})\mathrm{d}\xi_\alpha = \mathrm{d}\varphi(\vec{\xi}) \tag{27}$$

_is an exact differential._

The integrating factor $\lambda(\vec{\xi})$ is nonunique, since if $\mu(\varphi)$ is any differentiable function of $\varphi$, then $(\mathrm{d}\mu/\mathrm{d}\varphi)\mathrm{d}\varphi = \mathrm{d}\mu$ is also an exact differential. Thus $1/\bar{\lambda} \equiv \mu'/\lambda$ is also an integrating factor for (26), with $\mathrm{d}\bar{\varphi} \equiv \mu'(\varphi)\mathrm{d}\varphi$ the corresponding exact differential [53].

Recalling the previously stipulated requirements, Caratheodory's theorem may be applied to the first law (14) for a _locally adiabatic increment_ with $\mathbf{a} = \bar{\mathbf{a}}$(fixed) [5–7,20,57,106], based on the inaccessibility statement (25) of the second law:

$$\frac{1}{\lambda(\mathbf{E}, \vartheta; \bar{\mathbf{a}})}[\rho_0 \mathrm{d}u - \tilde{\mathbf{T}} \cdot \mathrm{d}\mathbf{E}]_{\mathbf{a}=\bar{\mathbf{a}}} = \mathrm{d}\varphi(\mathbf{E}, \vartheta; \bar{\mathbf{a}}) \tag{28}$$

By considerting the special cases of two or more mutually equilibrated systems in thermal contact, it is found (e.g. [6,53,56,106]) that $\lambda$ for any system must possess a common factor dependent only on $\vartheta$, this factor being therefore independent of any individual system. The symbol $\theta$ is used for the required form of this common factor, which is the absolute temperature; it must be a single-valued, monotonic function of a single sign (positive by convention), and is unique to within a multiplicative constant [51,53,56,58]. If for simplicity we choose unity for the remaining components of $\lambda$ for each system, the exact differential function of state $d\varphi(\mathbf{E}, \vartheta; \bar{\mathbf{a}})$ directly provides the differential entropy per unit reference volume ([53]; cf. [8,56,106]). Recognizing that for any value of $\bar{\mathbf{a}}$ there corresponds a state function hypersurface $\varphi$, and replacing the empirical temperature $\vartheta$ by the absolute temperature $\theta$, the function $\eta(\mathbf{E}, \theta; \mathbf{a})$ is employed to represent the entropy per unit reference mass. The possible entropy functions lie between bounds[16] differing only by functions of $\mathbf{a}$ ([5,6]; cf. [36,47]). Consideration of homothermal, but otherwise heterogeneous, systems produces the conclusion for such systems that entropy is extensive[17] ([106]; c.f. [56]).

Identification of the heat source term $r$ with radiation may require consideration of multiple 'temperatures'

[59]. The same qualification applies to the treatments of Section 3.2.

Edelen [57] proposes frameworks of the general type presented here, while assuming a semi-additivity property for energies of conjoined systems. The absolute temperature may then depend on $\mathbf{a}$ as well as $\vartheta$, coupled with more general behaviors for $u$, $\psi$ and their derivatives than result here.

The internal variable frameworks of the present section will herein be referred to as **VNE** type, in accordance with the contribution dates of the authors (Valanis, Nemat-Nasser, Edelen) cited.

*3.3.1.1. Helmholtz free energy, entropy rate and second part of the second law.* The existence of the entropy function of state permits the derivation of associated potential functions. From (28) using the notation described above [20],

$$[\rho_0 \mathrm{d}u(\bar{\mathbf{a}}) - \tilde{\mathbf{T}}(\bar{\mathbf{a}}) \cdot \mathrm{d}\mathbf{E}] = \rho_0 \theta \mathrm{d}\eta(\bar{\mathbf{a}}) \tag{29}$$

where $u$, $\eta$ and $\tilde{\mathbf{T}}$ are functions of $(\mathbf{E}, \theta; \mathbf{a})$, and the notation $(\bar{\mathbf{a}})$ is used as a reminder that $\mathbf{a}$ is constant in Eq. (29).

Writing the differential expansion of the specific Helmholtz free energy $\psi(\mathbf{E}, \theta; \mathbf{a})$, Eq. (18), about a state $(\bar{\mathbf{E}}, \bar{\theta}; \bar{\mathbf{a}})$ produces, using Eq. (29):

$$\mathrm{d}\psi = \rho_0^{-1}\tilde{\mathbf{T}} \cdot \mathrm{d}\mathbf{E} - \eta \mathrm{d}\theta + (\partial\psi/\partial\mathbf{a})^\mathrm{T} \cdot \mathrm{d}\mathbf{a}, \tag{30}$$

recalling that the notation of Eq. (29) is consistent with the relations (when the derivatives exist)

$$\mathrm{d}u = \mathrm{d}u(\bar{\mathbf{a}}) + (\partial u/\partial\mathbf{a})^\mathrm{T} \cdot \mathrm{d}\mathbf{a} \tag{31}$$

$$\mathrm{d}\eta = \mathrm{d}\eta(\bar{\mathbf{a}}) + (\partial\eta/\partial\mathbf{a})^\mathrm{T} \cdot \mathrm{d}\mathbf{a} \tag{32}$$

Eq. (30) is a first-order Taylor series expansion of an *arbitrary* increment $\mathrm{d}\psi$; Eq. (29) relates terms associated with constant $\mathbf{a}$. From Eq. (30) it follows immediately that the existence of the free energy provides a local potential function for the stress and entropy:

$$\tilde{\mathbf{T}} = \rho_0(\partial\psi/\partial\mathbf{E})^\mathrm{T} = \rho_0 \partial\psi/\partial\mathbf{E} \tag{33}$$

$$\eta = -\partial\psi/\partial\theta \tag{34}$$

From Eq. (18), with (14), (30):

$$\rho_0\dot{\eta} = \frac{\rho_0}{\theta}(\dot{u} - \dot{\psi} - \eta\dot{\theta}) = \frac{\dot{Q}_0}{\theta} - \frac{\rho_0}{\theta}\left(\frac{\partial\psi}{\partial\mathbf{a}}\right)^\mathrm{T} \cdot \dot{\mathbf{a}} \tag{35}$$

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[16] The method of [5,6] to obtain bounds is based on the equivalent of Eq.(39)$_2$; the same method can be applied based on Eqs. (36), (38).

[17] The same arguments apply to Sec. 3.3.2–3.3.3. Note that the second law (25), applied locally, results in a local entropy function, independent of extensivity considerations.

Eq. (35) may be rewritten, using $(14)_2$, as the next two equations. Inequality (38) is postulated[18] [cf. (16), (21)ff., (23)ff.]:

$$\rho_0\dot{\eta} - \left[ -\text{DIV}\left(\frac{\vec{q}_0}{\theta}\right) + \frac{\rho_0 r}{\theta} \right] \equiv \rho_0 \gamma \tag{36}$$

$$\rho_0 \gamma = \frac{-\vec{q}_0^T \vec{\nabla}_0 \theta}{\theta^2} - \frac{\rho_0}{\theta}\left(\frac{\partial \psi}{\partial \mathbf{a}}\right)^T \cdot \dot{\mathbf{a}} \tag{37}$$

$$\rho_0 \gamma \geqslant 0 \tag{38}$$

where the gradient operator with respect to the reference coordinates is employed.

Eq. (36) may be integrated (assuming the required smoothnesses) over the system volume or any sub-volumes. The result is the difference between the entropy rate and its sources as a result of surface and volumetric heat input. Vanishing $\dot{\mathbf{a}}$ in Eq. (37) results in the Fourier inequality ([16], pp. 116–117), $-\vec{q}_0^T \vec{\nabla}_0 \theta \geqslant 0$, consistent with the commonly applied Fourier law of heat conduction.

If $\mathbf{a}$ and $\dot{\mathbf{a}}$ are independent[19] of $\vec{\nabla}_0 \theta$, setting $\vec{\nabla}_0 \theta = 0$ in (37) and (38) produces the following relation for the *internal dissipation $\sigma$*, which holds independent of the value of $\vec{\nabla}_0 \theta$ [52]:

$$\sigma \equiv \gamma + \frac{\vec{q}_0^T \vec{\nabla}_0 \theta}{\rho_0 \theta^2} = -\frac{1}{\theta}\left(\frac{\partial \psi}{\partial \mathbf{a}}\right)^T \cdot \dot{\mathbf{a}} \geqslant 0 \tag{39}$$

The terminology is consistent with Coleman's [15] hereditary functional treatment (Section 5.3). Eq. $(39)_2$ is associated with certain stability properties [7,52].

Note the assumptions producing the inequality $(39)_2$ are stronger than the statement that $\dot{\eta} \geqslant 0$ in locally adiabatic transitions. The latter statement follows directly from the local C–D–T–T inequality Eq. (38) with (36), or the equivalent (except for required smoothnesses) global form (15). *The C–D–T–T inequalities, Eq. (15), (36), (38), are adopted here as the second part of the second law;* they guarantee satisfaction of the requirement of the Caratheodory approach that states inaccessible along curves $\rho_0 \mathrm{d}u(\mathbf{\bar{a}}) - \mathbf{\tilde{T}} \cdot \mathrm{d}\mathbf{E} = 0$ (i.e., states of lower entropy) should exist in an arbitrarily small neighborhood of every state. The assertion assumes invertible state relations in the sense that $(\mathbf{E}, \theta; \mathbf{a})$ space may be equivalently replaced by $(\mathbf{E}, \eta; \mathbf{a})$ space.

### 3.3.2. State and dissipative deformation variables

Boley and Weiner (**BW**; [47]) apply Caratheodory's theorem within a different conceptual framework. The deformation rate is decomposed into a recoverable part $\dot{\mathbf{e}}$ and a dissipative part $\dot{\mathbf{d}}$. Only the recoverable deformation $\mathbf{e}$ enters the argument lists of the energy functions (i.e., $\mathbf{e}$ is a state variable). The first law [cf. (14)] becomes

$$\rho_0 \dot{u} = \mathbf{t} \cdot \dot{\mathbf{e}} + \mathbf{s} \cdot \dot{\mathbf{d}} + \dot{Q}_0; \tag{40}$$

$$u = u(\mathbf{e}, \theta). \tag{41}$$

$\mathbf{t}$ and $\mathbf{s}$ are appropriate conjugate forces. Eq. (41) indicates that the dissipative deformation affects $u$ through its effects on $\theta$ and on the partition of the total deformation. The heat supply, description with respect to the reference volume, and use of second-rank tensors are slight modifications of the BW treatment for consistency.

In analogy to the derivation of (28)–(29), an equation of state is obtained from the inaccessibility of arbitrarily nearby states during processes with conditions $\dot{Q}_0 = 0$ and $\dot{\mathbf{d}} = \mathbf{0}$. Two equations result:

$$\rho_0 \dot{u} = \mathbf{t} \cdot \dot{\mathbf{e}} + \rho_0 \theta \dot{\eta} \tag{42}$$

$$\rho_0 \theta \dot{\eta} = \mathbf{s} \cdot \dot{\mathbf{d}} + \dot{Q}_0 \tag{43}$$

Eq. (43) follows from (42) and (40). The free energy is still defined by (18), resulting in (34) and $\mathbf{t} = \rho_0(\partial \psi / \partial \mathbf{e})^T$. Definition (36) for $\gamma$ produces, with (38), (43) and $(14)_2$,

$$\rho_0 \gamma = \frac{-\vec{q}_0^T \vec{\nabla}_0 \theta}{\theta^2} + \frac{\mathbf{s} \cdot \dot{\mathbf{d}}}{\theta} \geqslant 0 \tag{44}$$

### 3.3.3. Combined approach

The approaches of Sections 3.3.1 and 3.3.2 establish the existence of entropy for many material models. However, certain models addressing inelastic behaviors (e.g. [17,21,60]) employ $\psi(\mathbf{e}, \theta; \mathbf{a})$, where $\mathbf{e}$ is the recoverable component of deformation and direct measures of inelastic or total deformation do not appear as state variables.[20] A decomposition of work as employed by BW is thus suggested. Internal state variables (VNE) are required independently of such a decomposition; they do not contribute to net work (the conjugate forces do not appear on the bounding surfaces), but affect the entropy and thus the energies. The desired features of the earlier frameworks can be combined, as follows.

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[18] Alternatively, an assumed accessibility condition for the deformation and internal variables, together with (25), yields nondecreasing entropy in locally adiabatic processes [7,56].

[19] See Section 5.3.

[20] The VNE approach can be applied given $\mathbf{F}^e(\mathbf{F}, \mathbf{F}^i)$; $\mathbf{F}^e, \mathbf{F}^i$ are the elastic and inelastic deformation gradients. When $\mathbf{F}^i$ refers to plastic deformation, such a relation is normally assumed. Lee [107] argues against plastic deformation (as opposed to its history) as a state variable.

The first law is given by (40).[21] Caratheodory's theorem with $\dot{d}_{ij} = \dot{Q}_0 = 0$ and $\mathbf{a} = \bar{\mathbf{a}}$ produces

$$\rho_0 du(\bar{\mathbf{a}}) - t(\bar{\mathbf{a}}) \cdot de = \rho_0 \theta d\eta(\bar{\mathbf{a}}); \tag{45}$$

$$u = u(e, \theta; \mathbf{a}); \quad \psi = \psi(e, \theta; \mathbf{a}). \tag{46}$$

where $(46_1)$ is a constitutive assumption. Expansion of the free energy about the state $(\bar{e}, \bar{\theta}; \bar{\mathbf{a}})$ produces, with (45), (31), (32),

$$\dot{\psi} = \rho_0^{-1} \mathbf{t} \cdot \dot{\mathbf{e}} - \eta\dot{\theta} + (\partial\psi/\partial\mathbf{a})^T \cdot \dot{\mathbf{a}}. \tag{47}$$

It follows immediately that

$$\mathbf{t} = \rho_0 (\partial\psi/\partial\mathbf{e})^T; \quad \eta = -\partial\psi/\partial\theta. \tag{48}$$

Thus the free energy relates the stress to the recoverable strain, as in, e.g. [17,32,35,47,61,62]. From (18), $\rho_0\theta\dot{\eta} = \rho_0(\dot{u} - \dot{\psi} - \eta\dot{\theta})$; with (40) and (47) it follows that

$$\rho_0\theta\dot{\eta} = \mathbf{s} \cdot \dot{\mathbf{d}} + \dot{Q}_0 - \rho_0(\partial\psi/\partial\mathbf{a})^T \cdot \dot{\mathbf{a}}, \tag{49}$$

$$\rho_0\theta\gamma = \mathbf{s} \cdot \dot{\mathbf{d}} - \frac{\vec{q}_0^T \vec{\nabla}_0 \theta}{\theta} - \rho_0 \left(\frac{\partial\psi}{\partial\mathbf{a}}\right)^T \cdot \dot{\mathbf{a}} \geqslant 0 \tag{50}$$

where (50) results from (49), (36) and (38). Note from (49) that the dissipative terms $(\mathbf{s} \cdot \dot{\mathbf{d}} + \dot{Q}_0)$ in the first law (40) may be prescribed as $[\rho_0\theta\dot{\eta} + \rho_0(\partial\psi/\partial\mathbf{a})^T \cdot \dot{\mathbf{a}}]$.

Considering thermoelastoplastic (rate-independent) materials, Casey [1] employs a procedure equivalent to VNE,[22] without directly employing Caratheodory's theorem. Relations similar to (47)–(50) are obtained by constructing path-independent entropy functions for homothermal ($\vec{\nabla}_0\theta = 0$) thermoelastic processes, yielding entropy functions parametrized by constant values of the internal variables. The assumed internal energy $\tilde{u}$ and free energy $\tilde{\psi}$ state functions therein include in their arguments the total strain $\mathbf{E}$ and plastic strain $\mathbf{E}^p$, as opposed to (46). The consequences are the replacement of the dissipative work rate $\mathbf{s} \cdot \dot{\mathbf{d}}$ in (49)–(50) by $-\rho_0(\partial\tilde{\psi}/\partial\mathbf{E}^p)^T \cdot \dot{\mathbf{E}}^p$, and replacement of the recoverable work rate $\mathbf{t} \cdot \dot{\mathbf{e}}$ in (47) by $\rho_0[(\partial\tilde{\psi}/\partial\mathbf{E})^T \cdot \dot{\mathbf{E}} + (\partial\tilde{\psi}/\partial\mathbf{E}^p)^T \cdot \dot{\mathbf{E}}^p]$, i.e. by $(\tilde{\mathbf{T}} \cdot \dot{\mathbf{E}} - \mathbf{T}^d \cdot \dot{\mathbf{E}}^p)$ where $\tilde{\mathbf{T}}$ is the 2nd Piola–Kirchoff stress and $\mathbf{T}^d$ is a dissipative conjugate force. We recall from (48) that the free energy $\psi$ relates stress to recoverable strain, whereas the analogous equation with $\tilde{\psi}$ relates stress to total strain.

The non-thermal (recall Section 3.3.1) state and dissipative variables in the present and previous sections

could be assumed of arbitrary numbers, as tensors, scalars, etc.; see e.g. [47].

## 4. Objectivity

Constitutive equations must be invariant under a change of frame. If a change of frame of the current (Eulerian, spatial) configuration is given by

$$\vec{y}^*(t^*) = \vec{c}(t) + \mathbf{Q}(t) \cdot \vec{y}(t) \tag{51}$$

$$t^* = t - a, \tag{52}$$

where $\mathbf{Q}(t)$ is a rigid rotation ($\mathbf{Q}^T\mathbf{Q} = \mathbf{I}$) and $a$ and $\vec{c}$ are constants, the dependent and independent vector and tensor variables of a constitutive equation must transform according to (e.g. [9])

$$\vec{v}^* = \mathbf{Q}(t)\vec{v} \tag{53}$$

$$\mathbf{T}^* = \mathbf{Q}(t)\mathbf{T}\mathbf{Q}^T(t) \tag{54}$$

$$\mathbf{F}^* = \mathbf{Q}(t)\mathbf{F} \tag{55}$$

where $\vec{v}$ and $\mathbf{T}$ are arbitrary vectors and second-order tensors, and $\mathbf{F}$ is the deformation gradient or other two-point tensor (indices referred to both current and reference configurations). Higher-order tensors transform similarly for each index, while scalars must be invariant. These are the conditions for *(Eulerian)* objectivity. On the other hand, quantities referred only to the initial configuration are unaffected by such Eulerian frame changes, e.g. $\mathbf{C}^* \equiv \mathbf{F}^{*T}\mathbf{F}^* = \mathbf{C}$ by (55) and thus $\dot{\mathbf{C}}^* = \dot{\mathbf{C}}$; such invariance is called *Lagrangean* objectivity by Ogden [63]. Thus if the unspecified quantities $\mathbf{t}, \mathbf{s}, \mathbf{e}, \dot{\mathbf{d}}, \mathbf{a}$ of Sections 3.3.2 and 3.3.3 have only indices referred to the initial configuration (i.e. the quantities are Lagrangean), the equations of those sections are invariant to changes of the Eulerian frame. If instead (e.g. [21]) the quantities are work conjugate per unit initial *volume* but are attached to e.g. the Eulerian *configuration* (e.g. the stress power per unit initial volume may be written $\vec{\mathbf{t}} \cdot \mathbf{D}$ where $\vec{\mathbf{t}} \equiv J\mathbf{T}$ is the Kirchhoff stress and $\mathbf{T}$ is the Cauchy stress), equations of the sections cited which involve rates are not yet objective. It should be noted that configurations intermediate to the reference and current configurations are possible (e.g. [61,64]).

Requiring constitutive equations to represent the same phenomena in two frames leads to restrictions on the constitutive functionals. For example, a rotated Eulerian stress $\mathbf{T}^*$ attached to a rotated body and deformation $\mathbf{F}^*$ must be described by the same functional (Section 5.3) which gives the Eulerian stress $\mathbf{T}$ with deformation $\mathbf{F}$ in the unrotated frame. If $\mathbf{h}$ is the functional for the stress $\mathbf{T}$, the result is (e.g. [66])

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[21] See [21,60] for illustration.

[22] The plastic strain appears in Casey [1] as an internal state variable. It does not affect the expression of the first law because of the presence there of the rate of total strain, as total strain is also a state variable in that treatment.

$$\underset{\tau=-\infty}{\overset{t}{\mathbf{h}}}(\mathbf{F}(\tau)) = \mathbf{Q}^{\mathrm{T}}(t)\left(\underset{\tau=-\infty}{\overset{t}{\mathbf{h}}}(\mathbf{Q}(\tau)\mathbf{F}(\tau))\right)\mathbf{Q}(t) \qquad (56)$$

for the general case of history-dependent $\mathbf{h}$.[23]

Special consideration must be given to the time rates of Eulerian quantities appearing in constitutive equations. *Objective rates* (ˆ) are defined based on the spin $\mathbf{w}$ of an Eulerian frame as follows (e.g. [65]), noting $\mathbf{F}$ transforms as does $\vec{v}$:

$$\hat{\vec{v}} = \dot{\vec{v}} - \mathbf{w}\vec{v} \qquad (57)$$

$$\hat{\mathbf{T}} = \dot{\mathbf{T}} - \mathbf{w}\mathbf{T} + \mathbf{T}\mathbf{w} \qquad (58)$$

Rates defined by Eqs. (57)–(58) transform according to (53)–(55) when the spin $\mathbf{w}$ transforms according to (Lee et al. [67] and Dafalias [64])

$$\mathbf{w}^* = \dot{\mathbf{Q}}\mathbf{Q}^{\mathrm{T}} + \mathbf{Q}\mathbf{w}\mathbf{Q}^{\mathrm{T}} \qquad (59)$$

where the dual vector of the quantity $\mathbf{A} \equiv \dot{\mathbf{Q}}\mathbf{Q}^{\mathrm{T}}$ is the angular velocity of the frame rotating according to $\mathbf{Q}(t)$ [9]. From the perspective of the specified rotating frame, the objective rates of (57)–(58) reduce to material derivatives.

For materials with oriented substructure (e.g. [21,60,64,65,68,69]) $\mathbf{w}$ is associated with the spin of the substructure, e.g. the lattice directions of a single crystal or the fiber directions of a composite material, which differs in general from the continuum spin $\mathbf{W}$ (antisymmetric part of $\mathbf{L}$). The inelastic part of $(\mathbf{W}-\mathbf{w})$ is a "plastic spin" [65], which requires a constitutive relation for its definition. The concept can be generalized (e.g. [64,70]) to include multiple spins and associated objective rates corresponding to multiple substructures, i.e. internal variables.

Xiao et al. [71] demonstrate that spin tensors $\mathbf{w} = \bar{\mathbf{W}}(\mathbf{B}, \mathbf{D}, \mathbf{W})$, with $\mathbf{B} = \mathbf{F}\mathbf{F}^{\mathrm{T}}$ the left Cauchy–Green tensor and $\mathbf{W}$ and $\mathbf{D}$ as defined previously, provide rates (58) which are objective for any time-differentiable Eulerian symmetric tensor field $\mathbf{T}$, iff

$$\bar{\mathbf{W}} = \mathbf{W} + \bar{\mathbf{P}}(\mathbf{B}, \mathbf{D}), \qquad (60)$$

where $\bar{\mathbf{P}}(\mathbf{B}, \mathbf{D})$ is an antisymmetric tensor-valued isotropic function. Xiao et al. [72] found that the deformation rate $\mathbf{D}$ is the objective log-rate of the Eulerian logarithmic strain (definitions in [72]).

## 5. Applications

### 5.1. Thermoelasticity

For a thermoelastic model, the free energy is assumed free of any irreversibilities or history effects, therefore from Section 3.3.1,

$$\psi = \psi(\mathbf{E}, \theta), \qquad (61)$$

and the stress and entropy are given by (33)–(34), directly satisfying the requirements of objectivity. An alternative approach employs (19). Starting from $\psi = \psi(\mathbf{F}, \theta)$, for example (e.g. [12]), the chain rule for $\dot{\psi}$, Eqs. (11) and (13) yield

$$\left(\rho_0^{-1}\mathbf{T}^0 - \left(\frac{\partial\psi}{\partial\mathbf{F}}\right)^{\mathrm{T}}\right)\cdot\dot{\mathbf{F}} - \left(\eta + \frac{\partial\psi}{\partial\theta}\right)\dot{\theta} - \frac{\vec{q}^{\mathrm{T}}\vec{g}}{\rho\theta} \geqslant 0, \qquad (62)$$

recalling the first Piola–Kirchoff stress (Eq. (9)). Requiring (62) to hold for arbitrary $(\dot{\mathbf{F}}, \dot{\theta})$ produces (34), Fourier' law, and

$$\mathbf{T}^0 = \rho_0(\partial\psi/\partial\mathbf{F})^{\mathrm{T}}. \qquad (63)$$

$\psi = \psi(\mathbf{F}, \theta)$ fails to satisfy the requirements of objectivity. Cauchy's theorem on invariant functions [12,73] shows that $\psi$ is a scalar invariant to Eulerian frame changes iff it depends on $\mathbf{F}$ only through its dot products on the Eulerian index, i.e. through $C_{\mathrm{KM}} \equiv F_{\mathrm{K}i}^{\mathrm{T}}F_{i\mathrm{M}}$ or functions thereof (e.g. $\mathbf{E}$), rendering $\psi(\mathbf{E}(\mathbf{F}), \theta)$ an isotropic function. Eq. (63) is therefore employed with $\psi(\mathbf{E}(\mathbf{F}), \theta)$ and the chain rule. It is then verified that $\mathbf{T}^0$ is objective. Equivalently, (53)–(55) may be applied directly to restrict functions representing the stress, leading to (56) without history dependence [9,12,66].

It should be noted that while incremental relations which follow by differentiation of (33) are path-independent as required for an elastic material, commonly used incremental relations are not [74,75]. Some approaches are discussed by e.g. Dafalias [65], Pereda et al. [76], Xiao et al. [72].

With $\mathbf{a}$ and $\dot{\mathbf{a}}$ absent, Eq. (50) produces the Fourier inequality. As remarked by Rivlin [77], a procedure analogous to that applied to the stress constitutive equation by Rivlin [66] can be applied to the heat flux to guarantee objectivity. The result is (see also Section 5.3)

$$\vec{q}(t) = \mathbf{F}\vec{K}(\mathbf{E}, \theta, \vec{g}_0), \qquad (64)$$

$$\vec{g}_0 \equiv \vec{\nabla}_0\theta \equiv \mathrm{GRAD}\theta. \qquad (65)$$

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[23] If Eq. (56) is written without history dependence, $\mathbf{h}$ is a so-called isotropic function; cf. [64,65]. The word 'isotropic' is unrelated to symmetry of the associated material, which may be anisotropic.

## 5.2. Thermoplasticity

As mentioned in Section 3.3.3, the thermodynamics of that section is compatible with a well-established class of models, e.g. [17] where such models are applied to small strain thermoviscoplasticity and (rate-independent) thermoplasticity. A similar group of rate-dependent models is thoroughly reviewed in [78]; Walker [79], Lindholm et al. [80] and Krempl [81] are additional reviews to be considered. Hall [21] casts the finite deformation thermoviscoplasticity development of Chaboche [48] within the Section 3.3.3 framework, and incorporates the plastic spin suggested by Dafalias [68]. The interested reader will find there and in [60] development omitted from this section. Chaboche [48] and Lemaitre and Chaboche [17] discuss a similar framework for damage mechanics. Nemat-Nasser [6] describes modeling of Valanis [82] based on a 'material time' measure, which may simulate either rate-dependent or rate-independent behaviors, and related considerations within the VNE context; a more recent source is Valanis [83]. Malvern [9] is an excellent source for overall modeling considerations in thermomechanics, as well as fundamental considerations related to plasticity. For excellent additional discussions of plastic spin, Dafalias [64] can be consulted. Citations of the aforementioned references, as well as others of the present article, should also be of interest.

## 5.3. Thermoviscoelasticity

For finite deformation thermoviscoelasticity, selected fundamental references are Biot [84,85](reviewed in Fung [86]), Schapery [87,88], Valanis [89], Coleman [15,90], Day [28,29] and Christensen [91]. The treatments of the first three authors are related to the irreversible thermodynamics mentioned in the introduction to Section 3.2. The subject is briefly introduced here, following instead the rational thermodynamics approach of Coleman [15,90], mainly as restated by Day [29]. Other than the work of Day [28,29] concerning entropy existence (Section 3.2; separate from the material described below), the cited references postulate entropy as a primitive variable (e.g. Section 3.1). Other approaches to entropy existence are discussed in Section 3.2. Coleman and Owen [11] and Coleman et al. [41] should be especially noted in relation to the present development; as described in Section 3.2 and Owen [42], a corresponding unified treatment deriving both global and local entropy from a global statement of the second law is not yet available. The second law consistent with the purposes of Section 5.3.2 requires (global or local): at any state, neighboring states exist which are inaccessible by adiabatic processes with internal variables fixed. Thus the local entropy results of Sec. 5.3.2 are obtained from a global statement of the second law. The same second law, with the first law expressed for subvolumes, also provides a global extensive entropy when

restricted to homothermal, but otherwise heterogeneous, conditions (c.f. [5,7], [106]).

Gurtin and Hrusa [92] consider the special case when local constitutive representations are defined by single-integral laws, i.e. functionals defined by single integrations over time. They deduce restrictions on a class of such representations which ensure a corresponding single-integral entropy, assuming absolute temperature as a primitive variable. Restrictions on heat flux functionals are addressed when reduced to dependence on $(\mathbf{F}(t), \theta(t), \vec{g}(t))$.

A VNE treatment will eventually be constructed here for consistency with the entropy existence arguments of Section 3.3. Initially, however, a treatment based on the dissipation inequality (Section 3.1) will be developed. The deformation $\mathbf{E}$ is employed[24] here from the outset [91], as it is invariant to rigid rotations of the Eulerian frame (Sections 4 and 5.1). The following definitions are employed:

$$\underset{\approx}{\Lambda} \equiv (\mathbf{E}(t), \theta(t)) \tag{66}$$

$$\underset{\approx}{\Lambda^t}(s) \equiv \underset{\approx}{\Lambda}(t - s), \quad s \in [0, \infty) \tag{67}$$

$$\underset{\approx}{\Lambda_{\mathrm{r}}^t}(s) \equiv \underset{\approx}{\Lambda}(t - s), \quad s \in (0, \infty) \tag{68}$$

$$\underset{\approx}{\Lambda_{\mathrm{d}}^t}(s) \equiv \underset{\approx}{\Lambda}(t - s) - \underset{\approx}{\Lambda}(t), \quad s \in [0, \infty); \quad \underset{\approx}{\Lambda_{\mathrm{d}}^t}(0) = \underset{\approx}{0}. \tag{69}$$

$$\underset{\approx}{\Gamma_1}(\mathbf{L}_1, \lambda_1) \cdot \underset{\approx}{\Gamma_2}(\mathbf{L}_2, \lambda_2) \equiv \mathbf{L}_1 \cdot \mathbf{L}_2^T + \lambda_1 \lambda_2 \tag{70}$$

$$\left| \underset{\approx}{\Gamma}(\mathbf{L}, \lambda) \right|^2 \equiv \underset{\approx}{\Gamma} \cdot \underset{\approx}{\Gamma} \equiv \mathbf{L} \cdot \mathbf{L}^T + \lambda^2. \tag{71}$$

Eqs. (70), (71) show the inner product definition and natural norm $|\cdot|$ for elements $\underset{\approx}{\Gamma} = (\mathbf{L}, \lambda)$ of the *history* vector space corresponding to a fixed time. $\underset{\approx}{\Lambda^t}(s)$ is the *total* history vector. The subscript $r$ in Eq. (68) is used to denote the restriction of the history to past times, $s > 0$; $\underset{\approx}{\Lambda_{\mathrm{r}}^t}(s)$ is the *past* history vector. $\underset{\approx}{\Lambda_{\mathrm{d}}^t}(s)$ is the *difference* history vector.

The constitutive postulates are expressed in the form of functionals depending on the entire history of deformation and temperature.[25] Accordingly, the free energy functional has the equivalent forms [90]

$$\psi(t) = \overset{\infty}{\underset{s=0}{\mathrm{p}}} (\underset{\approx}{\Lambda}, \underset{\approx}{\Lambda_{\mathrm{d}}^t}(s)) = \overset{\infty}{\underset{s>0}{\mathrm{p}}} (\underset{\approx}{\Lambda}, \underset{\approx}{\Lambda_{\mathrm{r}}^t}(s)) \tag{72}$$

The argument lists of (72) both include the information required to construct the entire history $\underset{\approx}{\Lambda^t}(\cdot)$, and are

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[24] Coleman [15,90] and Day [29] employ $\mathbf{F}$.

[25] Dependence on the present value of temperature gradient, [cf. Eq. (1)], is omitted from response functionals other than the heat flux, for reasons to be explained.

therefore equivalently general. The argument $(\cdot)$ is used when the entire domain of a function is involved, or to emphasize the function as opposed to a value for specific $s$.

The hereditary/functional approach involves an expansion of the response functionals about the current state.[26] Smoothness is expressed with a fading memory norm, which incorporates an *obliviator*, or *influence function*. The obliviator characterizes the rate at which a material's memory of previous deformations fades with time. An obliviator $h$ is a continuous, positive, monotone decreasing function such that [29,94]

$$\int_0^\infty h(s)^2 \mathrm{d}s < \infty. \tag{73}$$

The results are independent of the choice of obliviator ([29], p. 87; more general theories of fading memory are cited there). The obliviator appears in the norm $\|(\cdot)\|$, which must be finite, for elements of an associated Hilbert space (with similarly defined inner products):

$$\left\| \underset{\approx}{\Gamma} \right\| \equiv \left[ \int_0^\infty h(s)^2 \underset{\approx}{\Gamma}(s) \cdot \underset{\approx}{\Gamma}(s) \mathrm{d}s \right]^{1/2} \tag{74}$$

The obliviator progressively diminishes the effects of deformations for times increasingly distant from the present (increasing $s$). For small $\|\underset{\approx}{\Gamma}\|$ and $|\underset{\approx}{\Omega}|$, smooth functionals $\bar{f}$ possess expansions as follows:

$$\bar{f}(\underset{\approx}{\Lambda} + \underset{\approx}{\Omega}, \underset{\approx}{\Lambda}_r^t(\cdot) + \underset{\approx}{\Gamma}(\cdot)) = \bar{f}(\underset{\approx}{\Lambda}, \underset{\approx}{\Lambda}_r^t(\cdot)) + \partial_{\underset{\approx}{\Lambda}} \bar{f}(\underset{\approx}{\Lambda}, \underset{\approx}{\Lambda}_r^t(\cdot)) \cdot \underset{\approx}{\Omega}$$

$$+ \delta \bar{f}(\underset{\approx}{\Lambda}, \underset{\approx}{\Lambda}_r^t(\cdot) | \underset{\approx}{\Gamma}(\cdot))$$

$$+ o\left( \left| \underset{\approx}{\Omega} \right| + \left\| \underset{\approx}{\Gamma}(\cdot) \right\| \right)$$

$$\tag{75}$$

$$\lim_{|\underset{\approx}{\Omega}| + \|\underset{\approx}{\Gamma}(\cdot)\| \to 0} o\left( \left| \underset{\approx}{\Omega} \right| + \left\| \underset{\approx}{\Gamma}(\cdot) \right\| \right) / \left( \left| \underset{\approx}{\Omega} \right| + \left\| \underset{\approx}{\Gamma}(\cdot) \right\| \right) = 0 \tag{76}$$

The notation $\bar{f}(\underset{\approx}{\Lambda}, \underset{\approx}{\Lambda}_r^t(\cdot))$ is used to represent a functional $\bar{f}$ of the second type in Eq. (72); we will consider such representations almost exclusively. $\delta f$ is a first-order Frechet differential (e.g. [91,95,96]) a functional which is linear in the past history variation $\underset{\approx}{\Gamma}(s)$. Higher order terms are multilinear in $\underset{\approx}{\Gamma}(s)$. Functional $\bar{f}$, $\partial_{\underset{\approx}{\Lambda}} \bar{f}$ and $\partial \bar{f}$ are continuous in all of their arguments. Illustrated for $\bar{f}$, continuity provides that,

$$\bar{f}(\underset{\approx}{\Lambda} + \underset{\approx}{\Omega}, \underset{\approx}{\Lambda}_r^t(\cdot) + \underset{\approx}{\Gamma}(\cdot)) - \bar{f}(\underset{\approx}{\Lambda}, \underset{\approx}{\Lambda}_r^t(\cdot)) \to 0 \tag{77}$$

as $|\underset{\approx}{\Omega}| + \left\| \underset{\approx}{\Gamma}(\cdot) \right\| \to 0$. Admissible past history functions are absolutely continuous and belong to the previously described Hilbert space, and the value at $s = 0+$ exists. Almost everywhere [111], the derivative belongs to the Hilbert space, and Jacobian determinants and absolute temperatures are restricted to be positive. Admissible functions on the domain of present time are differentiable and similarly restricted. For functionals obeying Eq. (75) and having admissible arguments, and with $f(t) \equiv \bar{f}(\underset{\approx}{\Lambda}(t), \underset{\approx}{\Lambda}_r^t(\cdot))$, the following chain rule applies [94] (cf. [29]):

$$\dot{f}(t) = \partial_{\underset{\approx}{\Lambda}} \bar{f}(\underset{\approx}{\Lambda}(t), \underset{\approx}{\Lambda}_r^t(\cdot)) \cdot \dot{\underset{\approx}{\Lambda}}(t) + \delta \bar{f}(\underset{\approx}{\Lambda}(t), \underset{\approx}{\Lambda}_r^t(\cdot) | \dot{\underset{\approx}{\Lambda}}_r^t(\cdot)) \tag{78}$$

Bounded motions which are sufficiently slow and continuous in the 'recent' past, for example, are associated with small norms in Eqs. (75)–(76) and may be accurately represented by the expansion about the current state (cf. [93], p. 245; [12], p. 109).

### 5.3.1. Dissipation inequality treatment

To affirm the conclusions of the VNE treatment, a development is first presented based on the dissipation inequality. Following Coleman [15] and Coleman and Mizel [4], employing constitutive functionals, and Coleman and Gurtin [52], employing internal variables with constitutive functions (Section 3.3), we initially add to the argument lists a potential dependence on the present value of the temperature gradient; here $\vec{g}_0(t)$ is equivalently employed instead of $\vec{g}(t)$. The conclusion is that only the heat flux $\vec{q}(t)$ may incorporate such dependence, hence its omission from earlier discussions. This is demonstrated here for the present functional treatment; the procedure for internal variable treatments is practically identical.[27] The constitutive functionals are thus expressed as [extending the smoothness assumptions to include the additional argument function $\vec{g}_0(t)$, and using referential quantities in (82) and (83) for convenience]:

$$\psi(t) = \bar{\psi}(\underset{\approx}{\Lambda}(t), \vec{g}_0(t), \underset{\approx}{\Lambda}_r^t(\cdot)) \tag{79}$$

$$u(t) = \bar{u}(\underset{\approx}{\Lambda}(t), \vec{g}_0(t), \underset{\approx}{\Lambda}_r^t(\cdot)) \tag{80}$$

$$\eta(t) = \bar{\eta}(\underset{\approx}{\Lambda}(t), \vec{g}_0(t), \underset{\approx}{\Lambda}_r^t(\cdot)) \tag{81}$$

$$\tilde{\mathbf{T}}(t) = \bar{\mathbf{T}}(\underset{\approx}{\Lambda}(t), \vec{g}_0(t), \underset{\approx}{\Lambda}_r^t(\cdot)) \tag{82}$$

$$\vec{q}_0(t) = \bar{\vec{q}}_0(\underset{\approx}{\Lambda}(t), \vec{g}_0(t), \underset{\approx}{\Lambda}_r^t(\cdot)) \tag{83}$$

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[26] Expansion about the current state suggests the use of current state as reference state, which involves relative deformation tensors [9]. For associated development see Coleman and Noll [93] and Truesdell and Noll [12].

[27] The present discussion considers derivatives of functionals; application of the method to functions is straightforward.

The dissipation inequality (19) is considered in the form [from (36), (38), (14), (18)]

$$\theta\gamma = -\dot{\psi} - \eta\dot{\theta} + \rho_0^{-1}\tilde{\mathbf{T}}\cdot\dot{\mathbf{E}} - (\rho_0\theta)^{-1}\vec{q}_0^{\mathrm{T}}\vec{g}_0 \geqslant 0. \tag{84}$$

Employing the chain rule (78) for $\dot{\psi}$ produces

$$\left[-\left(\frac{\partial\bar{\psi}}{\partial\mathbf{E}}(\underset{\approx}{\Lambda},\vec{g}_0,\underset{\approx}{\Lambda}_r^t(\cdot))\right)^{\mathrm{T}}+\rho_0^{-1}\bar{\mathbf{T}}(\underset{\approx}{\Lambda},\vec{g}_0,\underset{\approx}{\Lambda}_r^t(\cdot))\right]\cdot\dot{\mathbf{E}}$$

$$-\left(\frac{\partial\bar{\psi}}{\partial\theta}(\underset{\approx}{\Lambda},\vec{g}_0,\underset{\approx}{\Lambda}_r^t(\cdot))+\bar{\eta}(\underset{\approx}{\Lambda},\vec{g}_0,\underset{\approx}{\Lambda}_r^t(\cdot))\right)\dot{\theta}$$

$$-\left(\frac{\partial\bar{\psi}(\underset{\approx}{\Lambda},\vec{g}_0,\underset{\approx}{\Lambda}_r^t(\cdot))}{\partial\vec{g}_0}\right)^{\mathrm{T}}\cdot\dot{\vec{g}}_0$$

$$-\left(\delta\bar{\psi}(\underset{\approx}{\Lambda},\vec{g}_0,\underset{\approx}{\Lambda}_r^t(\cdot)|\dot{\underset{\approx}{\Lambda}}_r^t(\cdot))+\frac{\vec{g}_0^{\mathrm{T}}(t)\vec{q}_0(\underset{\approx}{\Lambda},\vec{g}_0,\underset{\approx}{\Lambda}_r^t(\cdot))}{\rho_0(t)\theta(t)}\right)\geqslant 0 \tag{85}$$

As $(\dot{\mathbf{E}}, \dot{\theta}, \dot{\vec{g}}_0)$ may be arbitrary (e.g. large magnitude with components of either sign), the inequality is guaranteed iff the coefficients of these terms vanish, and [recalling (65)]

$$\rho_0\gamma = -\frac{\vec{q}_0^T\vec{\nabla}_0\theta}{\theta^2} - \frac{\rho_0}{\theta}\delta\bar{\psi} \geqslant 0 \tag{86}$$

As $\partial\bar{\psi}/\partial\vec{g}_0$ must vanish, $\bar{\psi}$ (and $\delta\bar{\psi}$), and thus $\bar{\mathbf{T}}, \bar{\eta}, \bar{u}$ are independent of $\vec{g}_0$ as postulated earlier. $\vec{g}_0$ is thus henceforth omitted from the corresponding argument lists. The heat flux, of course, may still depend on $\vec{g}_0$, in accordance with Fourier's law. The equations relating the stress and entropy to the derivatives of the free energy follow from the first two terms of (85):

$$\tilde{\mathbf{T}} = \bar{\mathbf{T}}(\underset{\approx}{\Lambda},\underset{\approx}{\Lambda}_r^t(\cdot)) = \rho_0\left(\frac{\partial\bar{\psi}}{\partial\mathbf{E}}(\underset{\approx}{\Lambda},\underset{\approx}{\Lambda}_r^t(\cdot))\right)^{\mathrm{T}} \tag{87}$$

$$\eta = \bar{\eta}(\underset{\approx}{\Lambda},\underset{\approx}{\Lambda}_r^t(\cdot)) = -\frac{\partial\bar{\psi}}{\partial\theta}(\underset{\approx}{\Lambda},\underset{\approx}{\Lambda}_r^t(\cdot)) \tag{88}$$

Except for the argument lists and the presence of functionals rather than functions only, (87)–(88) appear strikingly similar to Eq. (33)–(34) of the VNE formulation of Section 3.3.1.

Eq. (39)$_1$ for the internal dissipation $\sigma$ is recalled, which defines the internal dissipation as the specific rate of production of entropy at zero temperature gradient [[15], Eq. (6.29)]:

$$\sigma \equiv \gamma + \frac{\vec{q}_0^{\mathrm{T}}\vec{\nabla}_0\theta}{\rho_0\theta^2} \tag{89}$$

$\delta\bar{\psi}$ is independent of $\vec{g}_0$. Setting $\vec{\nabla}_0\theta = 0$ in (86) produces the relation for the internal dissipation, to first order in the Frechet expansion, which holds independent of the value of $\vec{\nabla}_0\theta$ [4,15] in analogy to (39)$_2$:

$$\sigma = -\frac{1}{\theta}\delta\bar{\psi}(\underset{\approx}{\Lambda},\underset{\approx}{\Lambda}_r^t(\cdot)|\dot{\underset{\approx}{\Lambda}}_r^t(\cdot)) \geqslant 0 \tag{90}$$

Note that $\sigma$ *is independent of the present component* $\dot{\Lambda}(t)$ *of the history rate;* $\dot{\Lambda}(t)$ *is not associated with internal entropy production.* Another way to express definition (89) is as follows. From (36), (89), (14), and the rate form of (18) follows

$$\sigma = -\theta^{-1}(\dot{\psi} + \eta\dot{\theta} - \rho_0^{-1}\tilde{\mathbf{T}}\cdot\dot{\mathbf{E}}) \tag{91}$$

which is equivalent to Coleman [15], Eq. (8.1b)].[28] Eq. (87), (88) then produce the desired result:

$$\sigma = -\theta^{-1}\left(\dot{\psi} - \frac{\partial\bar{\psi}}{\partial\theta}\dot{\theta} - \left(\frac{\partial\bar{\psi}}{\partial\mathbf{E}}\right)^{\mathrm{T}}\cdot\dot{\mathbf{E}}\right)$$

$$= -\theta^{-1}(\dot{\psi} - (\partial_\Lambda\bar{\psi})\cdot\dot{\underset{\approx}{\Lambda}}) \tag{92}$$

*Thus $\vartheta\sigma$ is the negative of the component of $\dot{\psi}$ due to non-instantaneous (i.e. inelastic[29]) response; i.e., it is the magnitude of the rate of inelastic dissipation of free energy.* It is shown by Coleman [15, 90] that both sufficiently slow, and sufficiently fast, loading histories produce elastic behavior; the slope of the response of the latter depends upon the previous history. As argued by Rivlin (e.g. [8,97]) the latter characteristic results from the response functionals (72), (79)–(83) behaving as ordinary functions at the present time. As the contribution to the response functionals at time $t$ is given by a simple function of the strain and temperature at $t$, it is instantaneous; it can also be instantaneously removed. Thus, a differential increment of this contribution is instantaneous. As such responses are identified with elasticity, the interpretation of (92) follows, with the elastic part[30] of the free energy rate given by $(\partial_\Lambda\bar{\psi})\cdot\dot{\underset{\approx}{\Lambda}}$, the entire instantaneous contribution. It is observed that

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[28] Coleman's result follows from noting from Eqs. (7), (9) that $\rho_0^{-1}\tilde{\mathbf{T}}\cdot\dot{\mathbf{E}} = \rho^{-1}\mathbf{F}^{-1}\mathbf{T}\cdot\dot{\mathbf{F}} = \rho^{-1}\mathrm{tr}(\mathbf{F}^{-1}\mathbf{T}\dot{\mathbf{F}})$.

[29] The terminology is not meant to suggest that all elastic restorative forces are contained in the instantaneous response; they are not. A simple three-parameter solid, a spring in series with a unit consisting of another spring in parallel with a dashpot, is a counter-example. However, an agency applying load to a material behaving as a three-parameter solid can define the elastic part of the response only as that which occurs, and can be restored, instantaneously.

[30] It can be conversely noted that the difference occurring on the right side of Eq. (92) produces the internal entropy production, which is incompatible with elastic response.

(90) is recovered from (92) with the chain rule (78) for $\dot{\psi}$, which assumes a first-order Frechet expansion.[31]

The elastic behavior for quasistatic processes results from the assumption of fading memory; if the present value of $\Lambda \equiv (\mathbf{E}(t), \theta(t))$ is held for sufficient duration, the response depends only on that value. In the limit of infinitely slow processes, the effects of the past history vanish, i.e. the quasistatic and instantaneous responses coincide.

The importance of the present time and its association with static continuations is reflected by a non-zero Borel 'influence measure' at $s = 0$ ([4,99,100]; cf. [101]).

The functionals employed above are already invariant to rigid rotations of the Eulerian frame, i.e. they are Eulerian objective. If it is desired to express the stress or heat flux with respect to the Eulerian/current configuration, one need only employ the definitions (8) and (9) with (82) and (83), i.e.

$$\vec{q}(t) = J^{-1}\mathbf{F}\bar{\vec{q}}_0(\underset{\approx}{\Lambda}, \underset{\approx}{\Lambda}^t(\cdot), \vec{g}_0) \tag{93}$$

$$\mathbf{T}(t) = J^{-1}\mathbf{F}\bar{\mathbf{T}}(\underset{\approx}{\Lambda}, \underset{\approx}{\Lambda}^t(\cdot))\mathbf{F}^T \tag{94}$$

If the dependence on $J \equiv \det \mathbf{F} = [\det(2\mathbf{E} + \mathbf{I})]^{1/2}$ is incorporated into the functionals, (93)–(94) are equivalent to the forms indicated by e.g. [66,77], where the deformation variable employed was $\mathbf{C}$ instead of $\mathbf{E}$.

Linear viscoelasticity can be obtained by considering small strains and departures $\varphi \equiv \theta - \theta_0$ from the initital temperature. Strain and $\varphi/\theta_0$ are infinitesimals of $O(\varepsilon)$ with $\varepsilon = \underset{\tau}{\sup}|\mathbf{F}(\tau) - \mathbf{I}|$, where sup denotes the least upper bound; only terms of $O(\varepsilon)$ are retained in the constitutive relations. For example, the hereditary integral representation of $\psi$ is limited to second order in $(d\mathbf{E}, d\varphi)$, $\rho = \rho_0[1 + O(\varepsilon)]$ and $\mathbf{E} = \frac{1}{2}[\vec{\nabla}\vec{u} + (\vec{\nabla}\vec{u})^T] + O(\varepsilon^2)$, where $\vec{u}$ is the displacement vector [91].

Lustig et al. [98] reformulate the development of Coleman [15] based on 'material time,' which scales the response in such a way as to extend the viability of the expansion about the current state. The material time depends on the histories of the deformation and temperature. The free energy and internal dissipation are of second order in a Frechet expansion about the zero difference history, in accordance with the final footnote of the previous discussion.

### 5.3.2. Caratheodory basis for entropy and absolute temperature

To introduce a VNE formulation, it is noted that the following relationship is ultimately desired:

$$\psi(t) = \bar{\psi}(\underset{\approx}{\Lambda}(t), \underset{\approx}{\Lambda}^t_r(\cdot)) = \tilde{\psi}(\mathbf{E}(t), \theta(t); a(t)), \tag{95}$$

where $a(t)$ is a set of internal variables, which may be infinite in number. The function $\tilde{\psi}$ implies here a VNE treatment ($\mathbf{E}$ measures total deformation) and thus entropy existence. Recalling $\underset{\approx}{\Lambda}(t) = (\mathbf{E}(t), \theta(t))$, Eq. (95) immediately suggests the past history function as an internal variable (or it may be viewed as a continuum of internal variables, corresponding to variations of $s$ at fixed $t$);

$$\underset{\approx}{a}(t) \rightarrow \underset{\approx}{a}^t_r(s) = \underset{\approx}{\Lambda}^t_r(s) = \underset{\approx}{\Lambda}_r(t - s), \quad s \in (0, \infty) \tag{96}$$

We recall that the deformation can be viewed as having two components: an elastic component which occurs instantaneously at the present time, and a dissipative component which involves the history of the past rates of the thermomechanical variables. A simple visualization device is a thermoelastic spring in series with a dissipative element having non-instantaneous response. For a polymeric material, the spring may be viewed as associated with an instantaneous component of polymer coil extension, while the dissipative element is associated with relative motions of polymer chains, viscosity, and restorative forces which are restrained by these influences (e.g. a spring in parallel with a damper).

Internal variables fitting the VNE prescription are held constant while a reversible increment $(d\mathbf{E}(t), d\theta(t)) = (\dot{\mathbf{E}}(t), \dot{\theta}(t))dt$ is produced, which makes possible the application of Caratheodory's theorem. The reversible increment, which involves only quantities at the present time, does not affect the past history; i.e., quantities depending only on the past history are suitable internal variables for the Caratheodory framework.

The VNE treatment is thus initiated by assuming

$$u(t) = \bar{u}(\underset{\approx}{\Lambda}(t), \underset{\approx}{\Lambda}^t_r(\cdot)) = \tilde{u}(\underset{\approx}{\Lambda}(t); \underset{\approx}{a}^t_r(\cdot)) \tag{97}$$

where $\underset{\approx}{a}^t_r(s)$ is given by (96); the notation is employed as a reminder that a VNE internal variable treatment is being developed.

It is clear that $\tilde{u}$ is a functional, as the entire history is required, and the chain rule (78) applies to the functionals of the present treatment when their smoothness agree with those of Section 5.3.1. $\bar{\mathbf{T}}, \tilde{\mathbf{T}}$ refer below to the second Piola–Kirchhoff stress functionals in the two representations; dependence on empirical temperature $\vartheta$ is initially assumed.

Eq. (29) for the reversible increment[32] (application of Caratheodory's theorem) becomes

$$[\rho_0\dot{\tilde{u}}(\underset{\approx}{\bar{a}}^t_r(\cdot)) - \tilde{\mathbf{T}}(\underset{\approx}{\bar{a}}^t_r(\cdot)) \cdot \dot{\mathbf{E}}] = \rho_0\theta(\vartheta)\dot{\tilde{\eta}}(\underset{\approx}{\bar{a}}^t_r(\cdot)) \tag{98}$$

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[31] An expansion about the zero difference history (equilibrium) results in vanishing $\delta\bar{\psi}$ ([15], Eqs. (8.22); Lustig et al. [98], Eqs. (3.5) and (3.13)), requiring a second-order expansion and corresponding second-order internal dissipation.

[32] Note that because the functionals behave as functions at the present time, the same strategy applies globally.

$$[\partial_{\underset{\approx}{\Lambda}} \tilde{u} - \theta \partial_{\underset{\approx}{\Lambda}} \tilde{\eta}] \cdot \dot{\underset{\approx}{\Lambda}} = \rho_0^{-1} \tilde{\mathbf{T}} \cdot \dot{\mathbf{E}} \qquad (99)$$

where a time displacement d$t$ may be imposed across both sides if desired to replicate the context of (29), $\underset{\approx}{a}_{\mathrm{r}}^t(\cdot) = \underset{\approx}{\bar{a}}_{\mathrm{r}}^t(\cdot)$ is constant during the increment, and (99) is equivalent to (98). Given the existence of entropy and absolute temperature from (98)–(99), the required smoothnesses are assumed for application of the chain rule (78); the free energy rate is then expanded from (18) as

$$\dot{\tilde{\psi}}(\underset{\approx}{\Lambda}, \underset{\approx}{a}_{\mathrm{r}}^t(\cdot)) = [(\partial_{\underset{\approx}{\Lambda}} \tilde{u}) \cdot \dot{\underset{\approx}{\Lambda}} + \delta \tilde{u}(\underset{\approx}{\Lambda}, \underset{\approx}{a}_{\mathrm{r}}^t(\cdot) | \dot{\underset{\approx}{a}}_{\mathrm{r}}^t(\cdot))]$$
$$- \theta[(\partial_{\underset{\approx}{\Lambda}} \tilde{\eta}) \cdot \dot{\underset{\approx}{\Lambda}} + \delta \tilde{\eta}(\underset{\approx}{\Lambda}, \underset{\approx}{a}_{\mathrm{r}}^t(\cdot) | \dot{\underset{\approx}{a}}_{\mathrm{r}}^t(\cdot))]$$
$$- \tilde{\eta} \dot{\theta} \qquad (100)$$

by applying the chain rule to $\dot{\tilde{u}}, \dot{\tilde{\eta}}$. The definition of free energy (18) and the linearity of the Frechet differential [95,96] provide

$$\delta \tilde{u}(\underset{\approx}{\Lambda}, \underset{\approx}{a}_{\mathrm{r}}^t(\cdot) | \dot{\underset{\approx}{a}}_{\mathrm{r}}^t(\cdot)) - \theta \delta \tilde{\eta}(\underset{\approx}{\Lambda}, \underset{\approx}{a}_{\mathrm{r}}^t(\cdot) | \dot{\underset{\approx}{a}}_{\mathrm{r}}^t(\cdot))$$
$$= \delta \tilde{\psi}(\underset{\approx}{\Lambda}, \underset{\approx}{a}_{\mathrm{r}}^t(\cdot) | \dot{\underset{\approx}{a}}_{\mathrm{r}}^t(\cdot)) \qquad (101)$$

Eqs. (99)–(101) produce, in analogy to (30):

$$\dot{\tilde{\psi}} = \rho_0^{-1} \tilde{\mathbf{T}} \cdot \dot{\mathbf{E}} - \tilde{\eta} \dot{\theta} + \delta \tilde{\psi}(\underset{\approx}{\Lambda}, \underset{\approx}{a}_{\mathrm{r}}^t(\cdot) | \dot{\underset{\approx}{a}}_{\mathrm{r}}^t(\cdot)). \qquad (102)$$

Eqs. (33)–(34) for the stress and entropy are therefore recovered, providing then also from e.g. (91) or (92) that $-\theta^{-1}\delta\tilde{\psi}$ is the internal dissipation $\sigma$. From the definition (89), non-negative $\gamma$, and $\delta\tilde{\psi}$ independent of $\bar{\nabla}_0 \theta$, follows $\sigma \geqslant 0$. The VNE construction based on (96)–(97) thus provides the same results as the dissipation inequality treatment of the previous section, while establishing the existence of entropy and absolute temperature.

It is not the case that any practical internal variable model may be represented by a functional model meeting the previous description, or vice-versa. Rate-independent plasticity models, for example, may be written to yield $\dot{\mathbf{a}}(\mathbf{E}, \theta, \mathbf{a}, \dot{\mathbf{E}}, \dot{\theta})$ for the evolution of the internal variables, i.e. the entire histories of the controllable variables appear (referring to (1) without $\bar{g}$-dependence), with their *present* rates, which therefore enter the internal dissipation (39). Common viscoplasticity models give $\dot{\mathbf{a}}(\mathbf{E}, \theta, \mathbf{a})$, i.e. neither the present or past controllable rates are explicitly[33] required and are therefore absent from the internal dissipation. It is nevertheless the case that behaviors of functional models may be mimicked

by the described common internal variable models, and vice-versa, under practical and restricted circumstances.

Rivlin [8,97] considers application of a Caratheodory-based method to materials with memory. Processes considered are limited to those which begin and end in states of thermomechanical equilibrium, as in Day [29]. Entropy is defined as the state function, associated with a quasistatically thermoelastic body, derived from Caratheodory's theorem for reversible (quasistatic) processes. The same function of state is employed to assign values to the entropy at the equilibrium start and end states of such a body. Entropy at an instant during an irreversible process is considered undefined. By considering a system containing reservoirs transmitting and receiving heat reversibly to and from the body, a Clausius–Plank inequality [a time-integrated analogue of (15)] is deduced. Additional arguments involving approximate and physical motivations are presented.

### 5.4. Composite materials

Deformations of composite materials may be modeled in various ways as arising from the contributions of constituent materials behaving in accordance with the previously developed principles of thermomechanics. Further details are beyond the scope of the present study. Many outstanding authors contribute to the modeling of thermoelastic and thermoinelastic behaviors in composites; two sources will be mentioned in particular due to their strong relationships to previous developments. Tiersten and Jahanmir [102] apply the BW [47] thermodynamics to a finitely deformable, heat conducting composite modeled as a mixture of $N$ interpenetrating phases with viscous dissipation; wave propagation is the motivation. Valanis [103] applies the VNE approach to anisotropic, inelastic, heat conducting materials with a material time measure, for small strains and temperature changes; a mechanical mixture theory is developed for the stiffness of an elastoplastic matrix, elastic fiber composite.

It is the author's pleasure to note on this occasion the volumes, Reddy JN., editor, *Mechanics of Composite Materials; Selected Works of Nicholas J. Pagano* [104], and Pagano NJ, editor, *Interlaminar Response of Composite Materials* [105], which survey often-cited, fundamental and lasting contributions to the understanding of the thermomechanical behaviors of composite materials.

### 6. Conclusion

Constitutive model formulation depends on the availabilities of entropy, internal energy and associated potentials. An attempt has been made here to summarize some of the key contributions to the literature. The Caratheodory constructions provided in this work offer

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[33] Explicit knowledge of the histories of the controllable variables, as indicated by Eq. (1), provides also the rates at which the paths were traversed.

another means to justify the existence of entropy for the specified classes of models, subject to the assumptions detailed in Section 3.3. Favorable aspects of these methods include: the absence of cyclic processes, bounded operators or presumed accessibilities in the statement of the second law (the Caratheodory statements rest instead on *inaccessibility* under adiabatic conditions); global and local statements of the second law are naturally related; entropy production is not required to vanish at the quasistatic limit; thermoelastic, thermoplastic and thermoviscoelastic phenomena are all admitted.

It is experiments which ultimately justify the methods described. There are a wide range of thermodynamic models, in fields such as thermoelasticity, thermoplasticity, thermoviscoelasticity, phase changing materials, thermo-electromagnetoelastic materials, shock waves, biomaterials, composite materials, etc., at infinitesimal and finite strains, for static and dynamic motions, which employ potentials and kinematics based on principles discussed here. Although there is much work to be done to attain the ultimate level of understanding, much work exists which points to the acceptability of the underlying assumptions for engineering applications.

More complicated subjects incorporating additional coupled phenomena have not been addressed here, e.g. multi-component mixtures with processes of diffusion and chemical reactions; substantiating the associated models is obviously more difficult. Yet, growing confidence in approaches for simpler systems obviously extends in part to more complex systems which include the simpler systems as components.

## Acknowledgements

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